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THE SYNTHESIS OF BORON CARBIDE FILAMENTS

3rd QUARTERLY REPORT

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SPACE SCIENCES LABORATORY

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SUMMARY

This Third Quarterly Report is a presentation of the progress made during the latest reporting period of NASA Contract NASw-670 concerned with the synthesis of boron carbide filaments. As reported previously[1,2] B_4C filaments have been grown and progress has been made toward ascertaining their strength and crystal structure. Continued improvement has been made in the length and number of whiskers which can be produced utilizing the pure vapor method. Whiskers, whose lengths approach 8mm, have been grown reproducibly. Further attempts to grow B_4C whiskers by the dynamic flow method have not proved fruitful. Although whisker like crystals can be produced, to date, they do not compare in quality and quantity with the whiskers grown by the pure vapor method. It was hoped that a final decision concerning the choice of methods could be made at this time. However, the dynamic method (due to its apparent ease of control, etc.) will not be abandoned completely until all avenues of research have been investigated. Strength data has been accumulating and although testing of the filaments is a difficult task due to their length, significant progress has been made and will be presented. Continued studies on the morphology, orientation, crystal structure, etc. of B_4C whiskers are paralleling the strength and growth work and will also be reported upon. Some wetting studies have been made in a preliminary attempt to choose a suitable matrix for composite fabrication. These results will be described.

Future work will include a continued effort to understand and control the growth of B_4C whiskers with the ultimate goal being the production of abundant quantities of "Good" strong, useful whiskers. Strength studies will continue and be directed toward understanding the mechanisms of strength inherent in the whiskers and will also attempt to discover any trends toward the strength of the whiskers to be influenced by orientation differences, size difference, etc. Material characterization is of course a continuing phase of this contract. The last quarter effort will emphasize the fabrication of composites containing B_4C whiskers.

I. INTRODUCTION

The purpose of this program is to synthesize boron carbide whiskers, to ascertain their mechanical properties, and to utilize such whiskers in metal based composites. The whisker concept of strength is well documented throughout the literature and is attributed to the whisker's crystalline perfection. Such super-strong crystals lead to the theory that if their inherent strength could be successfully utilized then a new class of high strength, high temperature materials would be available for exploitation. Sutton et al[3] have shown the feasibility of using such ultra-strength fibers in a metal composite; specifically alumina whiskers in a silver matrix. B_4C whiskers[1] can theoretically extend the temperature and strength capability versus that of alumina composites by at least 30% due to B_4C's higher melting point and lower density. Such composites, when developed, can extend the present strength level of normal high temperature materials by an order of magnitude.

Continued improvement in the length, number and quality of B_4C whiskers has been noted. Sufficient quantities of whiskers will be available for small scale composite fabrication. An extensive study is in progress to evaluate the room temperature mechanical properties of B_4C whiskers. Young's modulus has been measured and approximates the value of 65×10^6 psi published in the literature. The crystal structure of some whiskers which had been pulled in tension have been determined and will be reported upon. More normal types of whiskers such as "a" types have been found. Whiskers of the rhombohedral type had been reported on previously[2]. Preliminary studies on the ability of various metals to wet B_4C have been made using a hydrogen atmosphere. These results will be discussed.

II. EXPERIMENTAL PROCEDURES AND RESULTS

The study has developed into a four-phased project. The growth phase has been directed toward producing adequate supplies of whiskers for the other study phases and for the ultimate goal of fabricating and testing composites. Optimization of process variables in terms of quality and physical characteristics of the B_4C whiskers is also a major part of the growth phase. Strength studies are a very important phase of this program. The strength characteristics of B_4C whiskers as a function of such variables as whisker orientation, diameter, temperature, etc. will be necessary in order to predict composite strengths and to eventually fabricate strong useful composites. The structure studies supplement both the growth and strength phases and also add to our basic scientific knowledge of fibrous composites. The final phase is the fabrication of metal-whisker composities. The goal of the composite study is the utilization of strong whisker components into large useful structural members of shapes. It is the phase which can justify the interest and work expended in this field and carries with it the promise of future super-tailor-made materials.

A. GROWTH OF B_4C WHISKERS

Continued emphasis during this quarter has been placed on growing boron carbide whiskers by the pure vapor method of deposition as described in the second quarterly report[2]. By increasing the amount of B_4C placed in a large "Lazy Susan" type material tray[2] from approximately 20 gm to more than 40 gms in present runs in the large vapor deposition furnace (previously described[1]) the population density and the average length of the B_4C whiskers produced has been greatly enhanced. Figure 1 shows a typical growth in a section of the deposition area. Optimum furnace conditions have remained the same, (i.e., 5 hours heat at 1900°C in the vaporization area). An increase in whisker length can be obtained by increasing the run time in the large furnace to 7.5 hours, however, this produces surface overgrowths on a significant number of the whiskers. Figure 2 shows an example of such an overgrown whisker.

The adapter previously described[2] which provided for the stacking of the two small vapor deposition furnaces has been constructed and installed. Figure 3 shows the completed installation. The furnace now can be operated with two different temperature zones. Unfortunately the present design allows a short but troublesome lower temperature to exist as a ring between the two furnaces. A modification is now being installed that should alleviate this condition.

An ATJ* graphite "Lazy Susan" shown in Figure 4 together with the double length reaction tube, was constructed for the stacked furnace. When loaded with approximately 10 gm of B_4C powder this furnace grows the same quality of whiskers as the large furnace. Because of the short cool section mentioned above, all the whisker growth at the present time occurs at the point of lowest temperature, the vapor not reaching the upper furnace. This is well illustrated in Figure 5. The modification envisioned will allow this small area to be expanded to the total area of the deposition tube thereby increasing the growth potential of the system. Although duplicate results have been obtained in both furnace geometries (i.e., large furnace vs small stacked furnaces) operating conditions are not identical. The small furnace requires a temperature of 2100°C in the evaporation zone compared with 1900°C in the large furnace. Deposition zone temperatures do appear to be similar however and approximate 1700°C. The deposition temperature will be definitely established once the extraneous temperature gradients are eliminated in the stacked furnaces.

Several runs have been made using the dynamic chemical method of gas phase vapor deposition. The feed materials to the stacked furnace were boron trichloride, methane and hydrogen. Flow rates and temperatures have been varied in an attempt to establish the proper growth environment. As yet only poorly characterized whiskers have been observed. Process studies of this method will be accelerated after the removal of the cold zone

*National Carbon Co.

in the stacked furnaces. Although many variables exist which make the pure vapor method feasible while the dynamic method remains elusive, the problems of diffusing species, atmosphere variations and impurity concentrations seem to be most important. It is hoped that the species problem can be controlled by pre-reaction at comparable temperatures with the evaporation temperature of the pure vapor process. Atmosphere variations arise due to the reacting gases such as $BCl_3 + CH_4$ forming gaseous HCl. This variable has not been assessed. It is becoming increasingly apparent that impurity concentrations within the bulk B_4C powder used during the pure vapor method exerts a large influence on the final whisker product. Since the gases used during the dynamic process are relatively pure and do not contain similar trace elements present in bulk B_4C, the impurity effect cannot be duplicated. Continued work in the subject of impurity effect on the growth of B_4C whiskers may lead to a clue as to what impurities, if any, are needed in the dynamic system to control the nucleation rate of whiskers.

B. MECHANICAL PROPERTIES OF B_4C WHISKERS

Additional data have been obtained on tensile properties of B_4C. The tests were performed on a Tecam Micro-Tensile Testing Machine, which was briefly described in the 2nd Quarterly Report[2].

All data obtained to date are shown in Table I. Specimens from six different furnace runs, each of varying quality, are represented. This batch variation undoubtedly contributes to the observed scatter. The effect of specimen size (cross-sectional area) on ultimate strength is shown in Figure 6. At present. the scatter in the data masks any size effect present.

The source of data scatter is due to several reasons. To date, the selection of a whisker for test has primarily depended on its length, because until recently only relatively short ones have been available. In this way, structurally imperfect whiskers (i.e., overgrowths, twists, etc) have been tested, and this fact is reflected in the results. With the recent availability of a larger population of longer whiskers, this factor may not be so pronounced in future work.

Another source of error is in the establishment of a cross-sectional area after fracture. The normal method of measuring this area after test is to photograph the fracture face at a known high magnification, cut out the fracture area from the photograph and weigh it. The area is calculated by making a comparative weighing of several one inch square specimens cut out from the same photograph. Figure 7 shows a typical fracture face of a tested specimen. The difficulty comes when the fracture surface is not perpendicular to the specimen axis, as shown in Figure 8. In this case, additional measurements must be made of the specimen by photographing the sides, with the attendant troubles of light reflection and the uncertainty of the location of the major dimensions. It is estimated that an error of about $\pm$ 30% is present in the fracture areas determined to date. The use of metallographic methods, involving the mounting of individual whiskers after test, is being investigated in an attempt to reduce this error.

Some difficulties have been encountered in measuring the elastic modulus of B_4C whiskers. As mentioned previously, early batches yielded short specimens (1/2 to 2mm long), which necessitated the use of very short gage lengths. The specimen is glued to fused silica holders with sym-diphenyl carbazide, and some elastic distortion of the diphenyl carbazide takes place during test. The consequence of short gage lengths is to obtain fictiously low values of the modulus because of the additional strain in the glue. This effect is shown in Figure 9. It appears, for the type whiskers encountered to date, that the true modulus is in the order of 65×10^6 psi. Modulii of this order were obtained from longer specimens.

It will be noted that only one specimen, #60-37a-9-7, had a strength approaching 10^6 psi. The reason for this high strength, as contrasted to the other specimen tested, is not known. It may well be due to lack of surface imperfections such as overgrowths, but if so this fact was not noticably evident on examination both before and after test.

TABLE I. SUMMARY OF B_4C WHISKER TENSILE DATA

Specimen No.	Total Length mm	Gage Length, mm	Area, μ^2	Apparent Elastic Modulus, psi	Ultimate Strength, psi	Cross Section	Whisker-Type (X-ray Diffract.)
60-37-68-1	2.0	0.25	292.0	19×10^6	350,000	Triangle	----------
60-37a-9-5	1.31	0.32	69.7	37×10^6	184,000	Triangle	----------
60-37a-9-6	0.73	0.14	75.5	22×10^6	315,000	"	----------
60-37a-9-7	2.77	0.72	66.4	71×10^6	934,000	Parallelogram	----------
60-37a-918	0.82	0.145	75.5	17×10^6	330,000	"	----------
60-37a-9-9	0.93	0.20	40.6	31×10^6	536,000	"	----------
60-37a-18-10	1.97	0.69	67.5	41×10^6	323,000	"	A
60-37a-18-11	0.55	0.15	12.2	31×10^6	350,000	"	----------
60-37a-18-12	0.67	0.21	7.4	23×10^6	615,000	"	----------
60-37a-25-13	2.27	0.26	542.0	24.5×10^6	>401,000	"	A
60-37a-25-14	3.04	1.10	99.3	67.1×10^6	573,000	"	A
60-37a-34-15	5.90	4.23	304.0	61.7×10^6	-----	"	----------
60-37a-36-16	4.21	2.05	169.0	76×10^6	179,000	"	----------

C. THE CRYSTAL CHARACTER OF B_4C WHISKERS

In the previous report period it was found that all of the short B_4C whiskers (less than 0.7 mm long) examined had their principal fiber axes parallel to either one or two of the rhombohedral unit cell edges. During this present report period, because of refinements in the growth procedure, longer B_4C whiskers (c.a. 2mm and longer) were made available for study. X-ray diffraction analysis of these longer fibers indicated: (a) that they were B_4C, (b) that they were single crystal and (c) that in each case, the major fiber axis was parallel to the a-crystallographic direction, $< 100 >$, of the hexagonal unit cell. Fibers for x-ray study were randomly chosen from various growth batches. In addition, the short fiber sections (approximately 0.5 mm long) remaining on the grips of the tensile tester, after tensile testing, were also analyzed.

The following method was found to be very satisfactory for handling and subsequently examining the short B_4C whisker sections which remained on the tensile tester grips. The short whisker fragments which were cemented onto the fused silica tensile grips with sym-diphenyl carbizide were first removed from the grips in an acetone bath. The fiber sections thus removed from the grips were then further washed in clean acetone and placed on a clean glass microscope slide. A small quantity of petroleum jelly was then placed on the tip of a fine (about 0.5 mm diameter) pyrex glass rod. The whisker section was carefully retrieved on the end of the glass rod tipped with petroleum jelly. The whisker was then manipulated so that its axis was roughly parallel to the glass rod. The glass rod and whisker combination was then positioned on the goniometer of a single crystal x-ray diffraction camera. The whisker was next properly oriented on the goniometer and finally photographed. All manipulations of the fiber during mounting was found to be best carried out under a low power binocular microscope.

In Figure 10 is shown an enlarged (2.2X) portion of an indexed x-ray diffraction photograph produced from a typical B_4C whisker. The well

defined spots indicate the single crystal character of the specimen. From measurements made on the separation distances of the 'layer-lines', y_1 and y_2, on the original diffraction photographs, and from a knowledge of the wavelength, λ, and radius, R, of the cylindrical diffraction camera, the repetition distance, p, along the axis of the fiber was reduced from the formula

$$p = m\lambda\left[1 + \left(\frac{R^2}{y_m^2}\right)\right]^{1/2} ,$$

where m = layer line number, m = 0, 1, 2, 3.....

It was thus determined that the repetion distance in all the long whiskers examined was 5.60 Å $\pm$ 0.02 Å. This distance compares very favorably with the literature[4] value for the length of the a-crystallographic edge of the hexagonal unit cell of B_4C, $a_o^* = 5.61$ Å. Hence, the fiber axis is parallel to the a-crystallographic direction. The external faces on the B_4C whiskers have not yet been identified.

A method for preparing surface replicas of fine B_4C whiskers - with cross sectional areas ranging between about $5\mu^2$ to $500\mu^2$ was developed late in the present report period. The specimen preparation method is as follows. A thin layer of cellulose acetate in acetone is spread uniformly on the inner face of the bottom piston of a conventional metallographic specimen embedding die. The whisker(s) of interest is positioned in the center of the piston, the die is filled with bakelite powder, assembled, pressured and heated in the manner which is standard in metallographic techniques. The cellulose acetate layer serves to hold the fiber(s) in position as well as to act as a cushion for the fiber(s) during pressing. After pressing and cooling, the die is opened and the specimen removed. The layer of cellulose acetate which is found to adhere to the bakelite mount may either be stripped mechanically or removed with acetone. The fiber(s) will then be found to be embedded in the bakelite with one face available for replication. The replica of the exposed face is prepared by

any of the well known methods of replica preparation, e.g., cellulose acetate in acetone. In Figure 11 is shown an electron photomicrograph of a replica produced from the surface of a B_4C whisker in the manner described above. The direction of the major axis of the whisker (a-crystallographic direction) is indicated by the arrow in this figure. The cellulose acetate primary replica after mechanical stripping was vacuum platinum shadowed, the shadowing angle being 45 degrees, and then vacuum coated with carbon vapor. The platinum shadowed carbon replica was removed from the cellulose acetate (primary replica) in acetone, dried, mounted on an electron microscope screen, and examined in the electron microscope (Hitachi HU-11). As may be seen in Figure 11 (magnification = 46,500X), the whisker face is not atomically smooth. The face contains oriented protrusions, parallel to the a-crystallographic direction, which vary in elevation from about 30 $\mathring{A}$ to greater than 3,000 $\mathring{A}$.

During the next report period, studies will continue on the surface and bulk perfection of B_4C whiskers. Correlations between whisker perfection and whisker strength will be investigated.

D. COMPOSITE STUDIES

Composite studies have begun and are presently concerned with the wetting properties of the metals copper, silver, gold, nickel and Fernico "5"(R) on Bulk B_4C. The wetting ability of liquids on solids can be described by the contact angle θ illustrated in Figure 12. Wetting can thus proceed from no wetting (90° contact angle) to complete wetting (0° contact angle). Data of this type is most easily determined by using the sessile technique. Experiments "in vacuum" in a sessile drop apparatus described by Sutton* (5) are now underway but no data are as yet available at this reporting period. Some preliminary experiments were performed in hydrogen atmosphere utilizing small pieces of B_4C and samples of the afore-

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*Work done on Army Contract No. Da-36-034-ORD-3768Z

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mentioned metals. Figure 13 and Table II are a compilation of this data. From these data it appears that nickel or Fernico "5" are the best wetters. More experiments will have to be done to elucidate these results.

TABLE II. SUMMARY OF PRELIMINARY EXPERIMENTS WITH B_4C AND VARIOUS METALS IN HYDROGEN ATMOSPHERE

Metal	Temp.	Time	Remarks (Contact Angle)
Silver	1100°C	1 hr.	$\theta > 90^\circ$
Copper	1100°C	1 hr.	$\theta > 90^\circ$
Gold	1100°C	1 hr.	$\theta > 90^\circ$
Nickel	1500°C	1 hr.	$\theta < 90^\circ$
Fernico "5"	1500°C	1 hr.	$\theta < 90^\circ$

III. CONCLUSIONS

1. Continual improvement in growth techniques have been evident during this quarter. The quantity and quality of B_4C whiskers now grown routinely exceeds those grown previously. There is mounting evidence that the process is very sensitive to impurities, therefore continued effort to understand the effect of these impurities in terms of type and concentration will be made.

2. The successful growth of significant quantities of B_4C whiskers of "Good" quality and adequate length has enabled the mechanical properties phase of the program to advance steadily. The Young's modulus of B_4C has been measured and is approximately 65×10^6 psi.

3. Material characterization has kept pace with the growth and mechanical properties studies with more normal growth types such as 'a' type whiskers being discovered.

4. The composite phase has begun with preliminary data factoring a matrix of either fernico "5" or nickel. However a final judgement will be made after more critical experiments are made in vacuum.

IV. FUTURE WORK

Routine runs will be made to furnish "Good" whiskers for continued studies on the mechanical properties, material characterization and composite fabrication. A most pressing problem in the growth phase is the classification of impurities and their effect on the growth process. Such techniques as the chemical and x-ray analysis of bulk B_4C samples before and after processing will be utilized.

Future work in the basic study of the strength of individual B_4C whiskers will be concentrated on the refinement of measurement techniques. Attempts will be made to pick structurally good whiskers in order to obtain upper limits on the strength of B_4C whiskers.

Structure studies will continue to parallel growth and strength studies. A concentrated effort will be made to elucidate more fully the morphology of B_4C whiskers made to date utilizing electron microscope techniques.

Wetting experiments in vacuum will be completed and a suitable matrix for composite fabrication will be chosen. Initial attempts will be made to fabricate composites and the resulting samples will be tested in tension.

ACKNOWLEDGEMENTS

Acknowledgement is given to Messrs. W. Laskow, C. Miglionico and T. Harris for their valuable assistance in this program.

REFERENCES

1. A. Gatti, R. Cree, E. Feingold, "The Synthesis of Boron Carbide Filaments" 1st Quarterly Report, October 10, 1963.

2. A. Gatti, R. Cree, E. Feingold, R. Mehan, "The Synthesis of Boron Carbide Filaments". 2nd Quarterly Report, January 10, 1964.

3. W. H. Sutton, and J. Chorne, A. Gatti, "Development of Composite Structural Materials for High Temperature Applications," 1st Quarterly through the 15th Quarterly Progress Reports, Contract NOw 60-0465d.

4. R. D. Allen, J. Amer. Chem. Soc., 75 3582 (1953).

5. W. H. Sutton, "Investigation of Bon ding in Oxide-Fiber (Whisker) Reinforced Metals, First Quarterly Report. Tech. Report, AMRA CR63-01/1.

Figure 1. Typical Grc B_4C Whiskers at 25X.

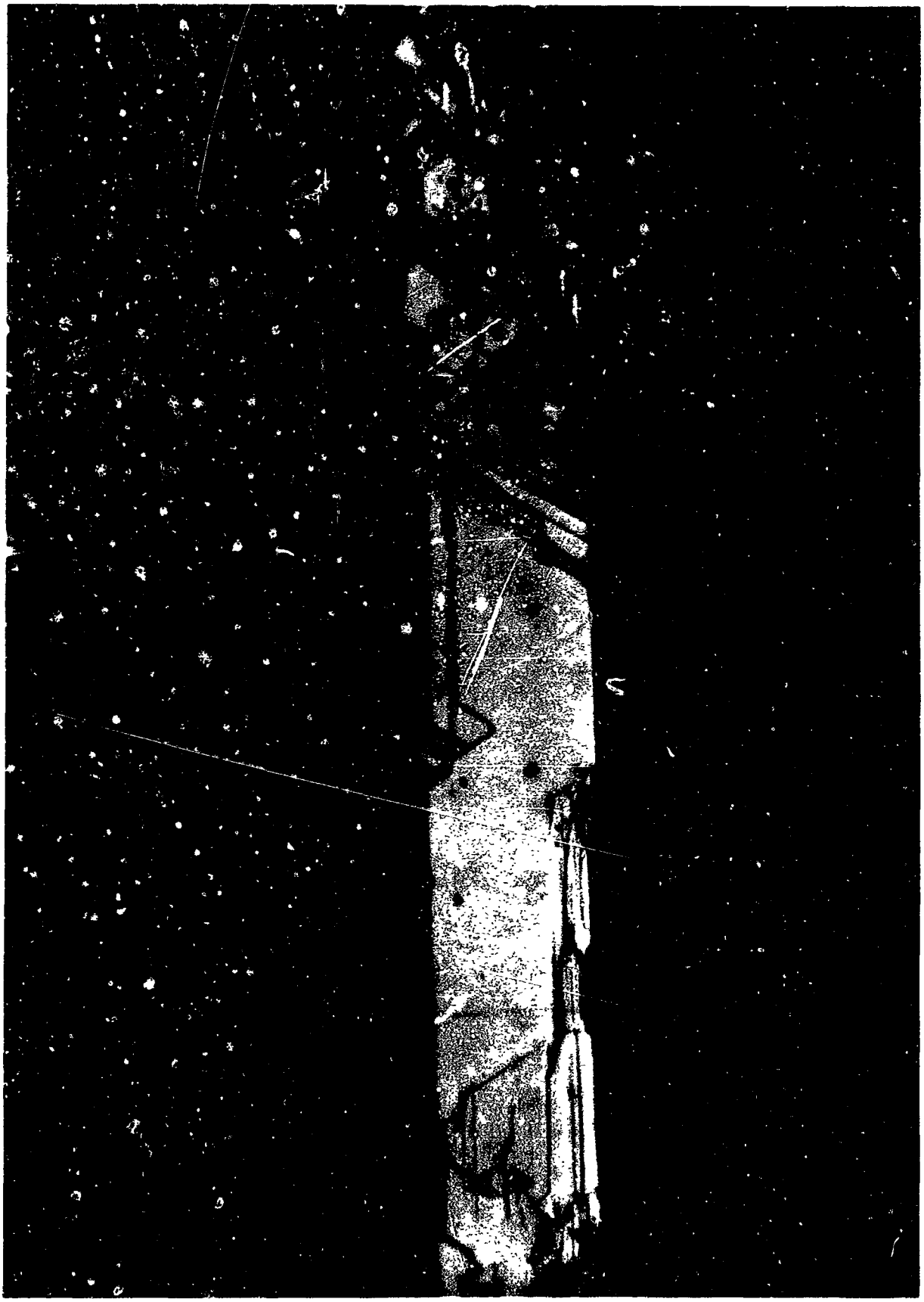


Figure 2. Photomicrograph of "overgrown" B_4C Whisker 650X.

Figure 3. Photograph of Stacked Furnace Assembly About 1/4 Size.

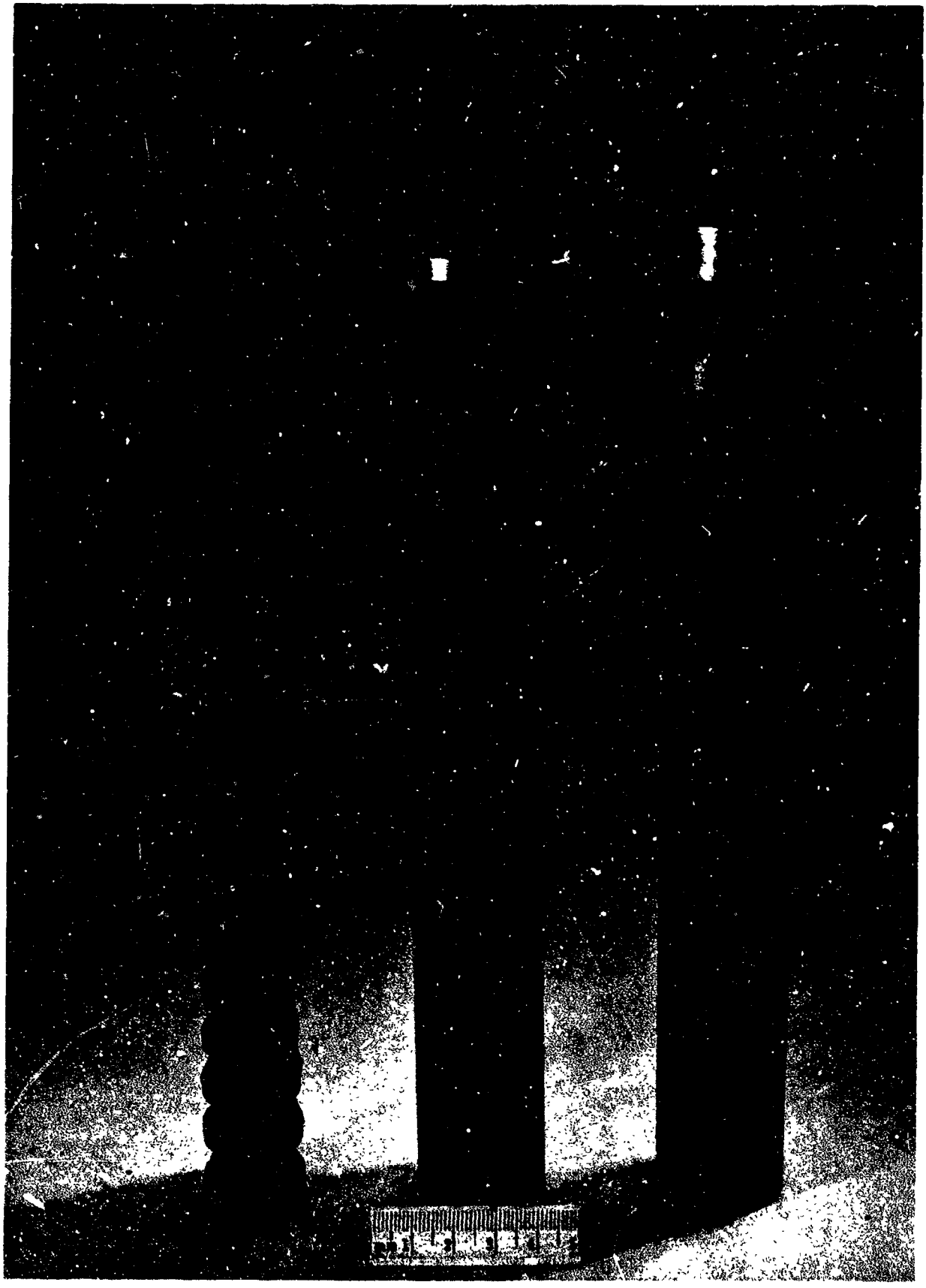


Figure 4. Photograph of "Lazy Susan" Tray and Deposition Tubes Used in Stacked Furnace Assembly.

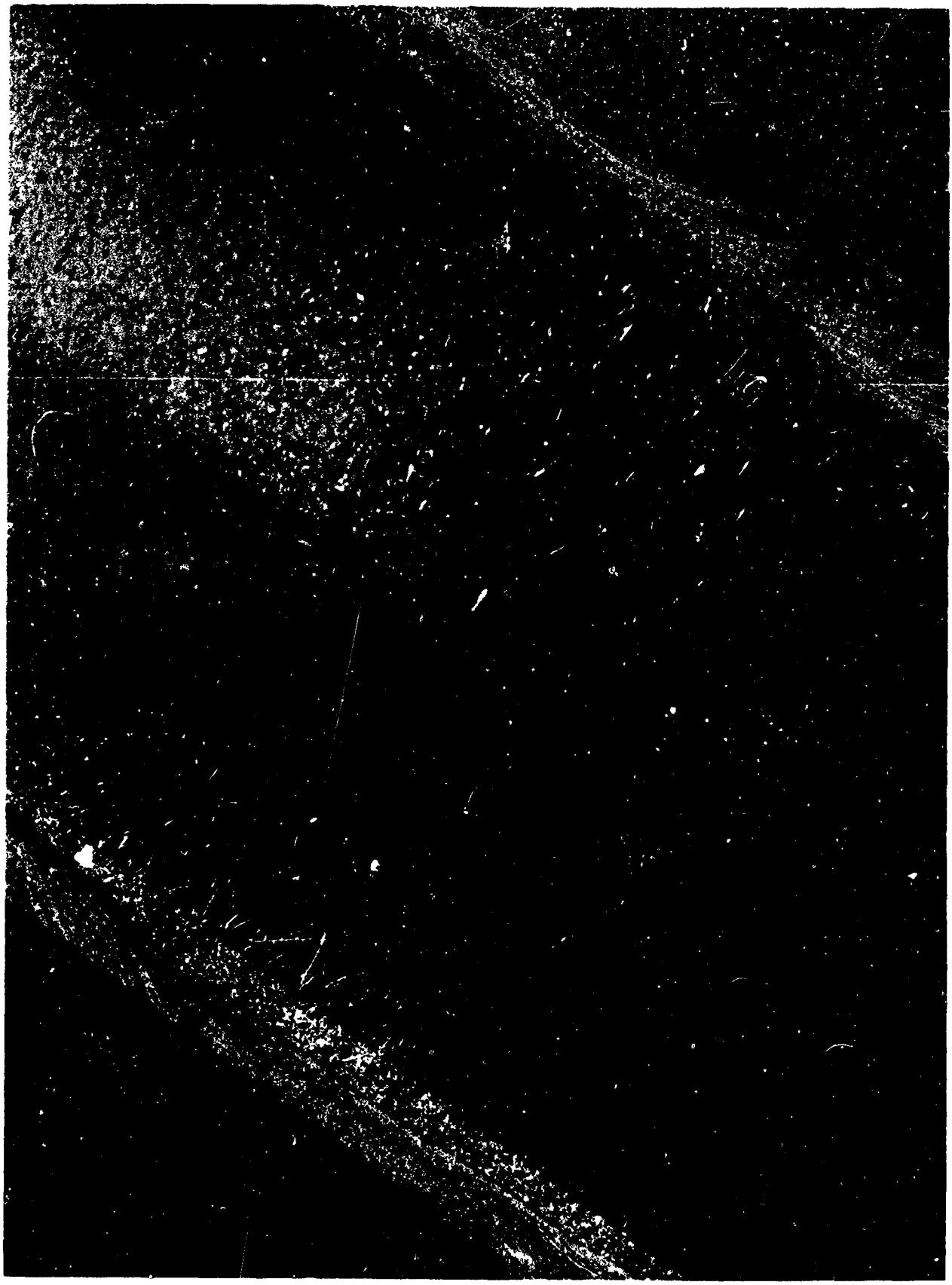


Figure 5. Illustration of Effect of Cool Section in Deposition Tube - 5X.

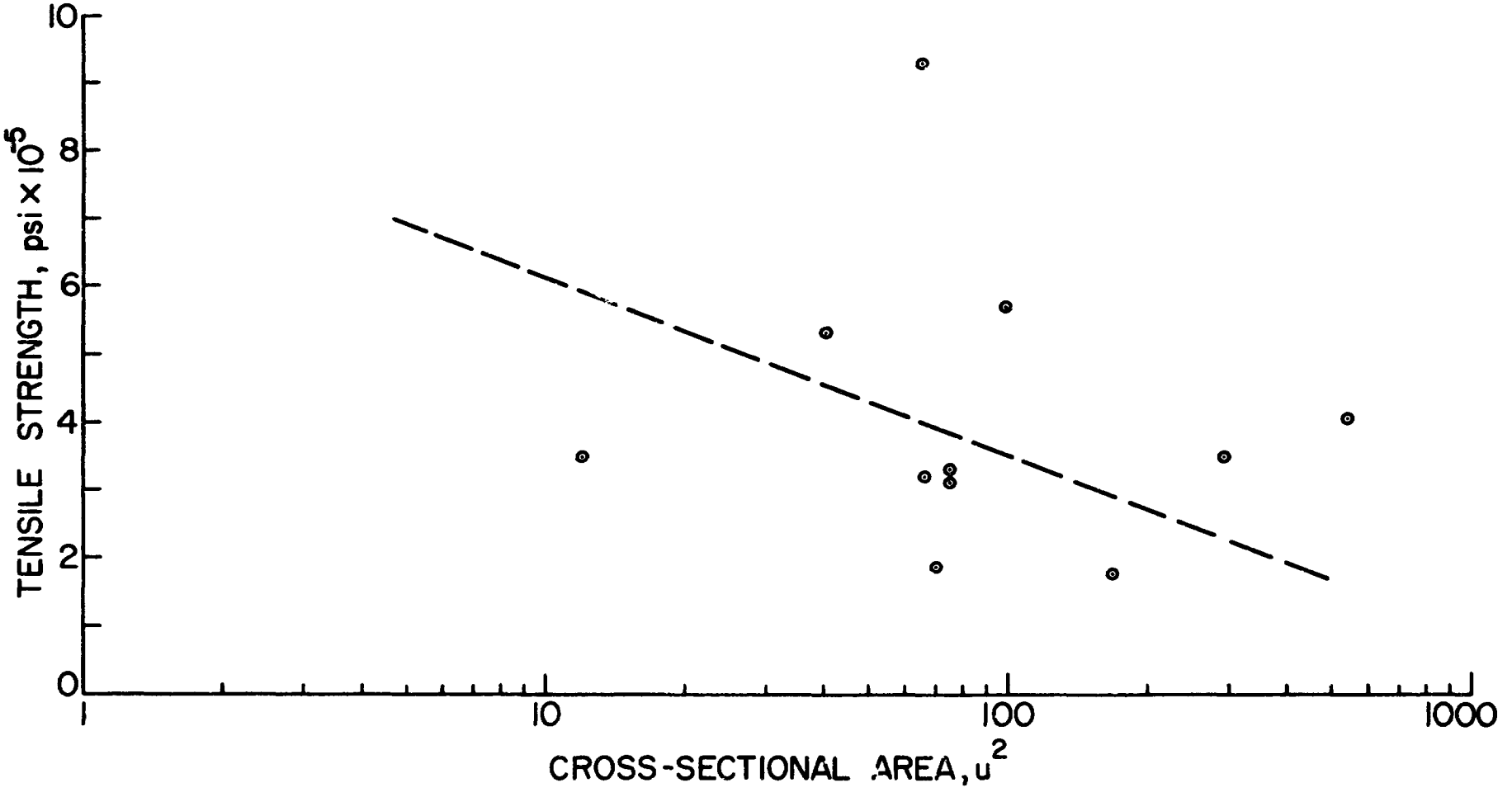


Figure 6. Tensile Strength of B_4C Whiskers as a Function of Area.

Figure 7. Typical Fracture Face of a Tested B_4C Whisker - 584X.

Figure 8. Longitudinal View of B_4C Whisker After Test - 350X.

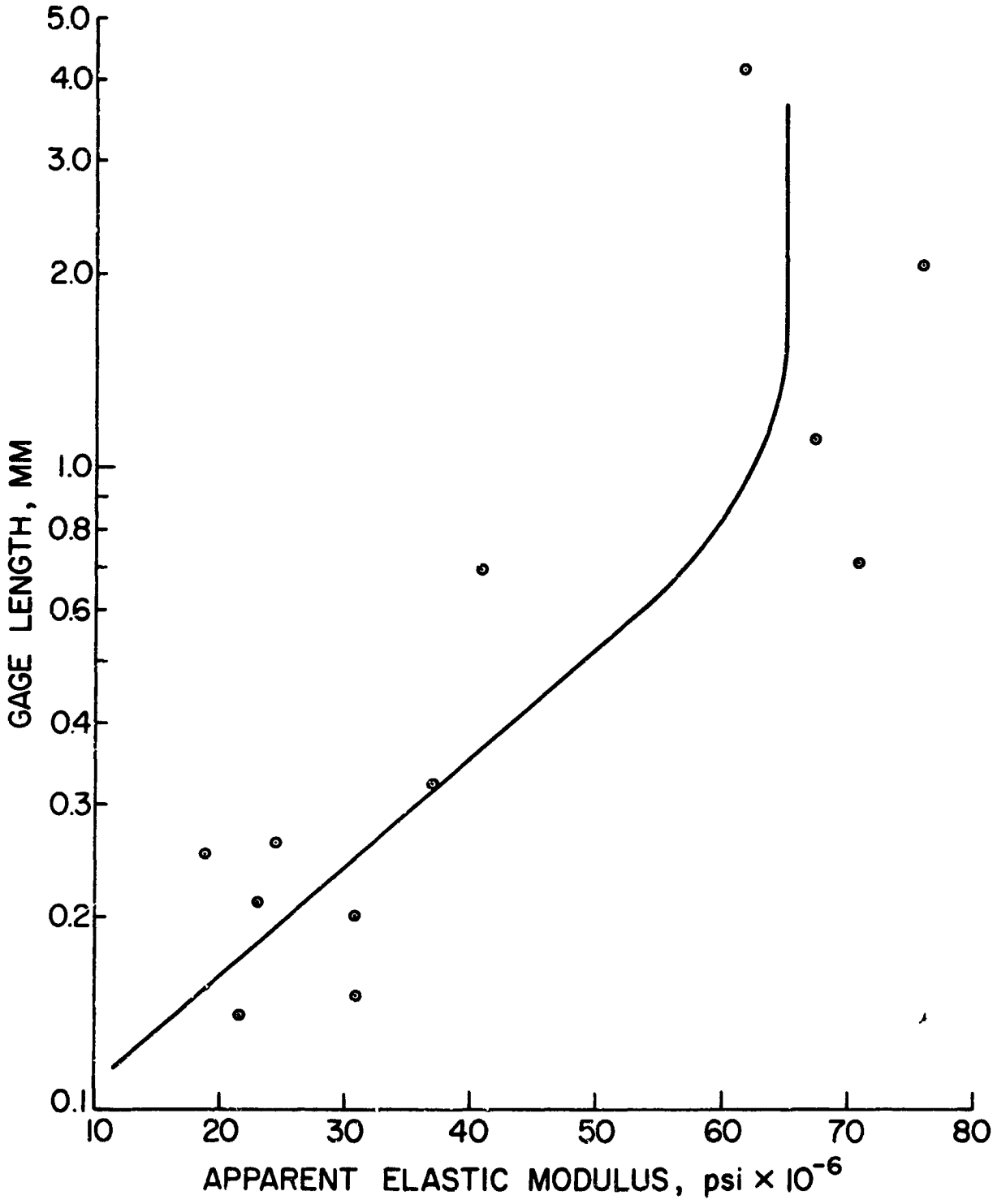


Figure 9. Apparent Elastic Modulus of B_4C Whiskers as a Function of Gage Length.

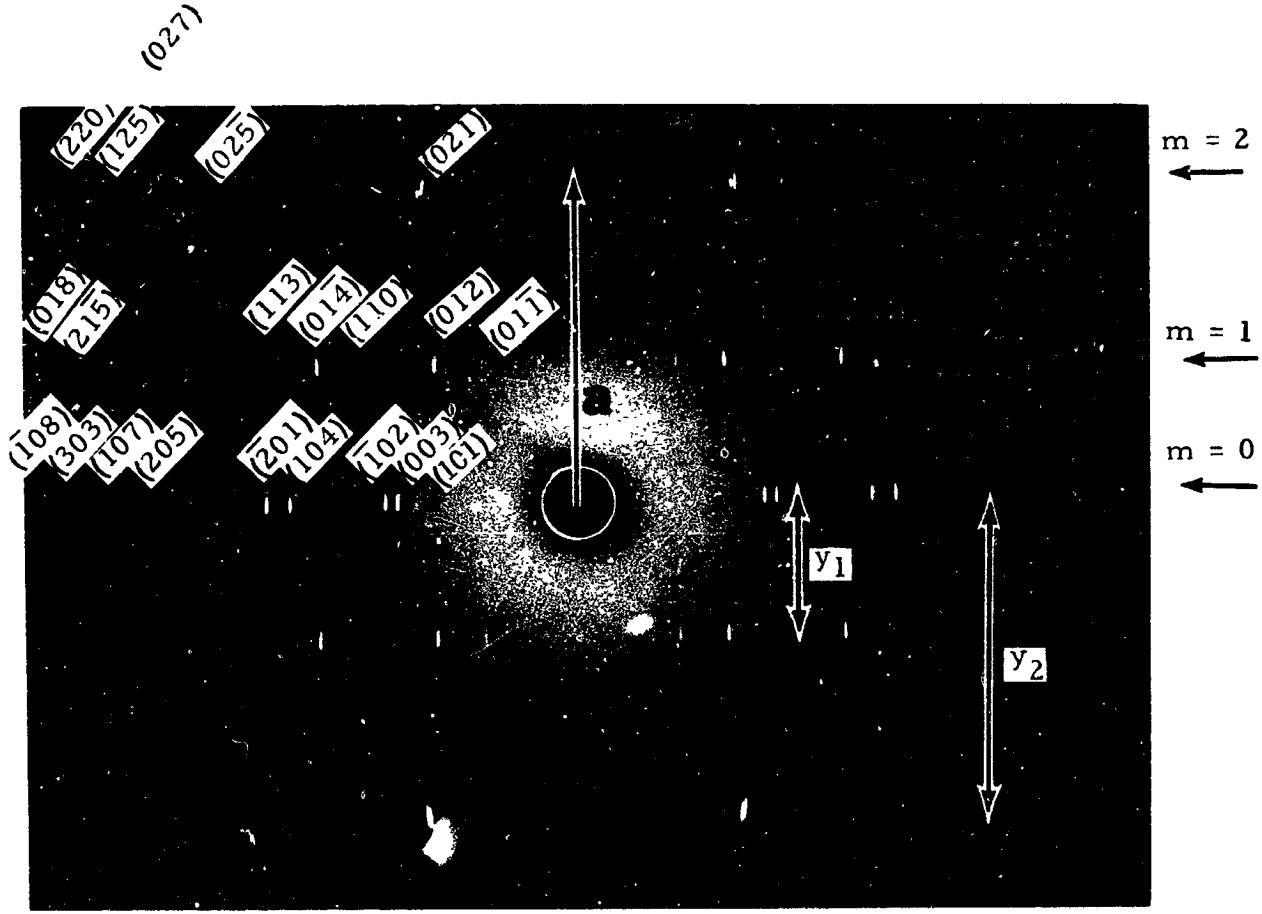


Figure 10. X-ray Diffraction Photograph (2.2X) of a Typical "a" Type B_4C Whisker.

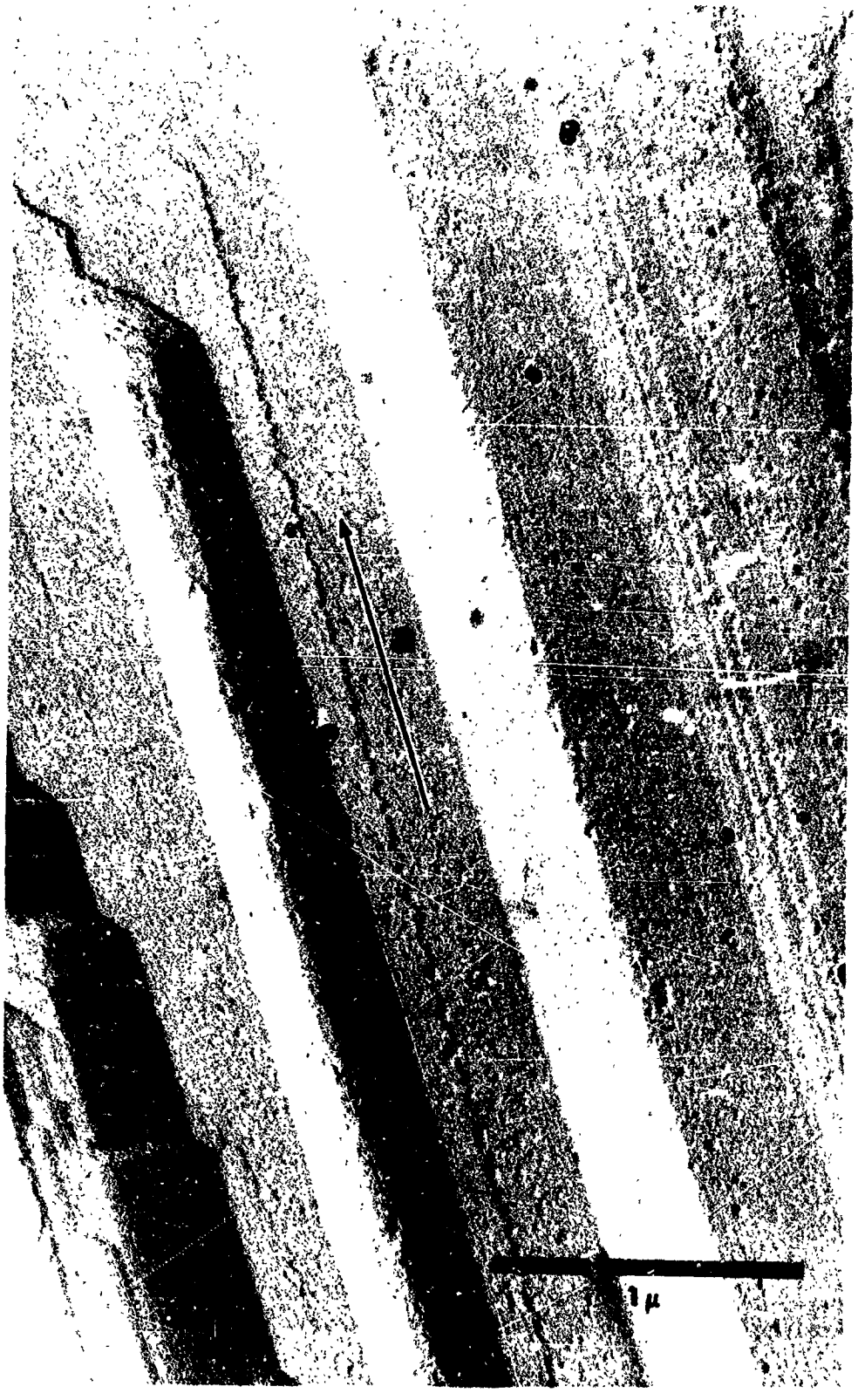
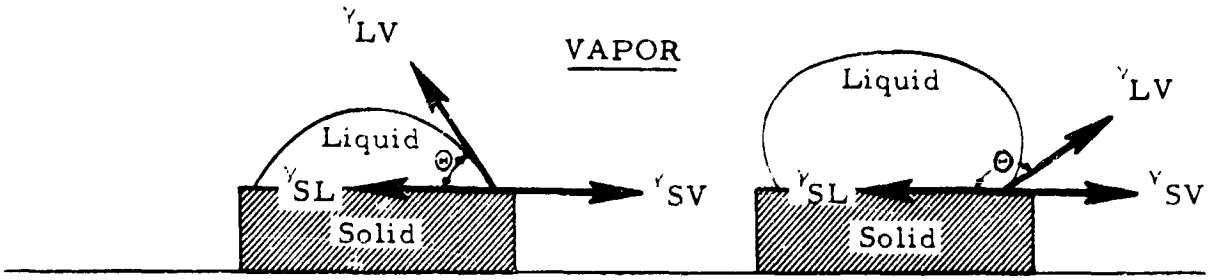


Figure 11. Electron Photomicrograph at 46,500X of the Surface of a B_4C Whisker. The Arrow Designates the Fiber Axis and the "a" Crystallographic Direction.

A. SOLID, LIQUID AND VAPOR UNDER EQUILIBRIUM CONDITIONS



(1) WETTING, $\Theta < 90^{\circ}$ (2) NON-WETTING, $\Theta > 90^{\circ}$

B. SYMBOLS

γ = surface energy (ergs/cm^2) for liquids; surface tension (dynes/cm)

Subscripts

S, L, V = solid, liquid, vapor

Θ = contact angle between solid-liquid and liquid-vapor interfaces

S = spreading coefficient; if S is positive, liquid will spread over solid surface

W = work of adhesion; the energy required to separate the liquid and solid at the interface

C. RELATIONSHIPS

$$\gamma_{SL} = \gamma_{SV} - \gamma_{LV} \cos \Theta \quad (1)$$

$$S_{SL} = \gamma_{SV} - (\gamma_{LV} + \gamma_{SL}) \quad (2)$$

for spreading; $\gamma_{SV} > \gamma_{LV} + \gamma_{SL}$ (3)

$$W = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \quad (4)$$

or $$W = \gamma_{LV} (1 + \cos \Theta) \quad (5)$$

Figure 12. Surface Energy Relationship Between Solid, Liquid and Vapor Interfaces from Sutton[5].

Figure 13. The Wetting of B_4C by the Metals (From Left to Right) Fernico 5, Nickel, Gold, Silver and Copper - 3X.